

FORM PTO-1390  
(REV. 11-94)U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

2988-694

10/018868

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)**

JUL 10 Rec'd PCT/PTO 19 DEC 2001

INTERNATIONAL APPLICATION NO  
PCT/FR00/01552INTERNATIONAL FILING DATE  
June 7, 2000PRIORITY DATE CLAIMED  
July 16, 1999 and August 9, 1999

## TITLE OF INVENTION

SUPPORTED METAL CATALYST, ITS PREPARATION AND ITS APPLICATIONS IN THE DIRECT MANUFACTURE OF HYDROGEN PEROXIDE

APPLICANT(S) FOR DO/EO/US  
Michel DEVIC

Applicant herewith submits to the United States Designated/ Elected Office (DO/EO/US) the following items under 35 U.S.C. 371:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the international Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
- ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureaus.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 37(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
- ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

International Publication WO 01/05501 A1  
International Preliminary Examination Report  
Form PCT/IB/306

INTERNATIONAL APPLICATION NO.  
PCT/FR00/01552

10/018868

INTERNATIONAL FILING DATE  
June 7, 200017. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees as follows:

CLAIMS				
(1)FOR	(2)NUMBER FILED	(3)NUMBER EXTRA	(4)RATE	(5)CALCULATIONS
TOTAL CLAIMS	27 -20	8	X \$18.00	\$ 136.00
INDEPENDENT CLAIMS	2 -3	0	X \$84.00	0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	<input type="checkbox"/>
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): <b>CHECK ONE BOX ONLY</b>				
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482)				
..... \$710.00				
<input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))				
..... \$740.00				
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO				
..... \$1,040.00				
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2) to (4)				
..... \$100.00				
<input checked="" type="checkbox"/> Filing with EPO or JPO search report				
..... \$890.00				\$ 890.00
Surcharge of \$130.00 for furnishing the National fee or oath or declaration later than 20 30 mos. from the earliest claimed priority date (37 CFR 1.492(e)).				
0			TOTAL OF ABOVE CALCULATIONS	= 1,026.00
Reduction by 1/2 for filing by small entity, if applicable. Affidavit must be filed also. (Note 37 CFR 1.9, 1.27, 1.28).				- \$ 0.00
0			SUBTOTAL	= 1,026.00
Processing fee of \$130.00 for furnishing the English Translation later than 20 30 mos. from the earliest claimed priority date (37 CFR 1.492(f)).				+
0			TOTAL FEES ENCLOSED	\$ 1,026.00

- a. ☐ A check in the amount of \$ 1,026.00 to cover the above fees is enclosed.
- b. ☒ Please charge Deposit Account No. 16-1150 in the amount of \$ 1,026.00 to cover the above fees. A copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 16-1150. A copy of this sheet is enclosed.

18. ☒ Other instructions  
Please calculate the fee after entering the Preliminary Amendment concurrently submitted.

19. ☒ All correspondence for this application should be mailed to  
PENNIE & EDMONDS LLP  
1155 Avenue of Americas  
New York, N.Y. 10036-2711

20. ☒ All telephone inquiries should be made to

Charles E. Miller  
NAME

SIGNATURE

24,576  
REGISTRATION NUMBER

December 19, 2001  
DATE

EXPRESS MAIL NO.:EL 477 033 071 US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application of: DEVIC

Group Art Unit: To be assigned

Serial No.: to be assigned

Examiner: To be assigned

Filed: Concurrently filed

Attorney Docket No.: 2988-694

For: SUPPORTED METAL CATALYST... New York, NY  
December 19, 2001

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Applicant respectfully requests entry of the following amendment and remarks in to the file of the above identified application.

**IN THE CLAIMS:**

Please cancel claims 1-14.

Please add the following new claims:

15. (New) A process for preparing a supported metal catalyst, comprising:
- (a) impregnating a support with a solution of a salt of a metal selected from the group consisting of palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold;
  - (b) subjecting the impregnated support to a reduction process; and
  - (c) treating the impregnated support obtained in step (b) with an aqueous acid solution containing bromine and bromide ions.

10018868-030702

16. (New) The process of claim 15, wherein the concentration of bromide ions in the aqueous acid solution is between about 20 mg/l and about 200 mg/l.

17. (New) The process of claim 15, wherein the concentration of bromide ions in the aqueous acid solution is between about 20 mg/l and about 100 mg/l.

18. (New) The process of claim 15, wherein the concentration of bromine in the aqueous acid solution is between about 2 mg/l and about 20 mg/l.

19. (New) The process of claim 15, wherein the concentration of bromine in the aqueous acid solution is between about 2 mg/l and about 10 mg/l.

20. (New) The process of claim 15, wherein the pH of the aqueous acid solution is between about 1 and about 3.

21. (New) The process of claim 15, wherein step (c) is conducted at a temperature between about 10 °C and about 80 °C.

22. (New) The process of claim 21, wherein the temperature is between about 40 °C and about 60 °C.

23. (New) The process of claim 15, wherein, the impregnated support obtained in step (c) is separated from the aqueous acid solution and dried at a temperature between about 100 °C and about 140 °C.

24. The process of claim 23, wherein, a slurry is obtained in step (a), which is filtered, drained and then dried before step (b).

25. The process of claim 24, wherein the drying is carried out under conditions conducive to slow crystallization.

26. The process of claim 15, wherein the metal-salt solution comprises two kinds of metal salts so that a supported bimetallic catalyst is obtained.

27. The process of claim 26, wherein the two kinds of metal salts are a majority metal salt and a minority metal salt, and the bimetallic catalyst comprises about 0.001 % to about 0.1 % by weight minority metal based on the weight of the bimetallic catalyst.

28. The process of claim 26, wherein the metal-salt solution contains salts of palladium and gold.

29. The process of claim 26, wherein the minority metal is platinum.

30. The process of claim 15, wherein the support is a silica having a BET specific surface area.

31. The process of claim 29, wherein the BET specific surface is greater than 200 m<sup>2</sup>/g.

32. A supported metal catalyst, which comprises  
a support and a metal selected from the group consisting of palladium,  
platinum, ruthenium, rhodium, iridium, osmium, holmium and gold, wherein the metal  
is disposed on the support in a form of cluster of crystals, and wherein the size of  
the cluster is between about 0.1  $\mu\text{m}$  and about 20  $\mu\text{m}$ .

33. The catalyst of claim 32, wherein the size of the cluster is between  
about 0.1  $\mu\text{m}$  and about 10  $\mu\text{m}$ .

34. The catalyst of claim 32, wherein the supported metal catalyst contains  
about 0.1 % to about 10 % by weight based on the weight of the catalyst.

35. The catalyst of claim 32, which is a supported bimetallic catalyst  
comprising two kinds of metals.

36. The catalyst of claim 35, wherein the two kinds of metals are a majority  
metal and a minority metal, and said catalyst contains about 0.001% to about 0.1 %  
minority metal by weight based on the weight of the catalyst.

37. The catalyst of claim 35, wherein the metals are palladium and gold.

38. The catalyst of claim 35, wherein the minority metal is platinum.

39. The catalyst of claim 32, wherein the support is a silica having a BET  
specific surface area.

40. The catalyst of claim 39, wherein the BET specific surface is greater than 200 m<sup>2</sup>/g.

41. A process for manufacturing hydrogen peroxide, wherein conducting a direct reaction between hydrogen and oxygen using the supported metal catalyst of claim 32.

**REMARKS**

Claim 1-14 has been canceled. Claims 15-41 have been added.

Support for the new claims can be found in the original specification, e.g., original claims. None of the amendment has narrowed scope of claims. No new matter is believed to be introduced.

No fee, other than that for the application filing fee, is believed due for the filing of this response. Should any fees be required, however, please charge such fees to Pennie & Edmonds LLP Deposit Account No. 16-1150.

Respectfully submitted,

Date: December 19, 2001



Charles E. Miller  
**PENNIE & EDMONDS LLP**  
1155 Avenue of the Americas  
New York, New York 10036-2711  
(212) 790-9090

24,576  
(Reg. No.)

Attorneys For Applicant

10018868-030702



**SUPPORTED METAL CATALYST, ITS PREPARATION AND ITS  
APPLICATIONS IN THE DIRECT MANUFACTURE OF HYDROGEN  
PEROXIDE**

The present invention relates to a supported metal catalyst suitable for the direct manufacture of hydrogen peroxide from hydrogen and oxygen. The subject of the invention is also the process for manufacturing the said catalyst and the process for manufacturing hydrogen peroxide using said catalyst.

The low productivity of the process for catalytic manufacturing of hydrogen peroxide directly from hydrogen and oxygen is an impediment to its development. There have been many attempts to improve this productivity. Mention may be made, for example, of US 3 336 112, US 3 361 533, US 4 007 526, US 4 009 252, US 4 279 883 and US 4 335 092. These studies are mainly based on a general concept, namely the stabilization of hydrogen peroxide using a sequestrate or a decomposition inhibitor.

Other ways of improving the hydrogen peroxide productivity of the direct process have also been explored. Thus, patent US 4 379 778 discloses a process for the direct manufacturing of hydrogen peroxide from hydrogen and oxygen in an aqueous medium containing decomposition inhibitors in the presence of a ~~palladium-carbon catalyst pretreated with an aldehyde~~

10018868-030702

or ketone and preferably also pretreated with a dilute hydrochloric acid solution.

The use of a bromide in the aqueous reaction mixture of the direct hydrogen peroxide manufacturing process is described in the patent US 4 772 458.

Finally, patents US 5 128 114 and US 5 352 645 describe a method of preparing catalysts based on palladium or platinum-palladium supported on non-agglomerated uniform porous silica microspheres which are attrition-resistant thanks to the use of ammonia citrate or of urea as additive and are suitable for the direct manufacture of hydrogen peroxide.

Example 12 of patent US 5 128 114 describes the preparation in two steps of a supported catalyst containing about 0.05% by weight of platinum and 1% by weight of palladium on porous silica microspheres. The support is firstly prepared by spray drying a mixture of Ludox AS 40 silica and urea, which is then calcined at 650°C in nitrogen. This support is then added to a solution of Pt and Pd, prepared beforehand by dissolving  $\text{H}_2\text{PtCl}_6$  and  $\text{PdCl}_2$  in water, heated to a temperature of between 60 and 70°C and acidified by concentrated HCl until a pH of about 1.2 is obtained. The resulting mixture is stirred, then spray dried and finally the powder obtained is reduced in a stream of hydrogen at 300°C.

The preparation of the supported catalyst according to Example 15 of patent US 5 352 645 is similar to that described in Example 12 of patent

10018868-030702

US 5 128 114 with, however, one difference. This is because the resulting mixture, instead of being spray dried, is vacuum dried at 100°C overnight and then the dried solid is reduced in a stream of hydrogen at 100°C. Metal crystallites of the order of 30 to 50 Å were thus obtained.

The filing company has developed a supported catalyst based on at least one metal selected from the group M formed from palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold and, in particular, a supported bimetallic catalyst. In general the supported bimetallic catalyst consists of a majority metal from the group M and a minority metal from the group M. The majority metal represents about 0.1 to 10% by weight of the catalyst and preferably between 0.5 and 1% by weight. The minority metal represents about 0.001 to 0.1% by weight of the catalyst and preferably between 0.01 and 0.05%.

Palladium and gold are advantageously selected as the majority metal.

Platinum and holmium are advantageously selected as the minority metal.

The supported bimetallic catalyst particularly preferred consists of palladium as the majority metal and platinum as the minority metal.

The subject of the invention is also a supported multi-metal catalyst consisting of a majority metal from the group M and of several minority metals from the group M. The preferred supported multi-metal

10018868-030702

catalyst comprises palladium as the majority metal and platinum and at least one metal from the group M as minority metals.

The majority metal content in the supported multi-metal catalyst is virtually identical to that of the bimetallic catalyst and each minority metal may be present in the catalyst in an amount representing about 0.001 to 0.1% by weight of the catalyst and preferably between about 0.01 and 0.05%.

The present invention furthermore provides a supported single-metal catalyst with, preferably, platinum or gold as the metallic constituent of the group M. The content of metallic constituent is in general between 0.1 and 10% by weight of the catalyst and preferably between 0.5 and 1% by weight.

Preferably, the supported metal catalyst according to the invention is characterized by clusters of crystallized metal or metals having a size of between 0.1 and 20  $\mu\text{m}$  and preferably between 1 and 10  $\mu\text{m}$ .

Silica, alumina, carbon and aluminosilicates may be suitable as support. However, it is preferred to use silicate, and advantageously silica particles having a mean size of between 1 and 50  $\mu\text{m}$ . It is also preferred to use silica having a BET specific surface area greater than 200  $\text{m}^2/\text{g}$  and usually between 300 and 600  $\text{m}^2/\text{g}$ . Aldrich's microporous silica referenced 28,851-9 has proved to be particularly useful.

---

The amount of iron (Fe) in the chosen support is preferably less than 0.001% by weight.

A second subject of the invention is a process for preparing a supported catalyst based on at least one metal from the group M defined above. This process, comprising, in succession, a step of impregnating a solution based on one or more salts of at least one metal, selected from the group M on a support and a reduction step, is characterized in that, after the reduction step, the catalyst is subjected to a treatment with an aqueous acid solution (A) containing bromine and bromide ions.

According to the present invention, the concentration of bromide ions in the aqueous solution (A) may be between 20 and 200 mg/l and preferably between 20 and 100 mg/l. The concentration of bromine ( $\text{Br}_2$ ) may be between 2 and 20 mg/l and preferably between 2 and 10 mg/l.

The pH of the aqueous solution (A) is preferably between 1 and 3.

The aqueous solution (A) may be prepared, for example, by dissolving an alkali or alkaline-earth metal bromide in water, then by adding bromine in bromine water form advantageously with a concentration close to 1% by weight and, finally, the pH may be adjusted using an acid. When the catalyst to be prepared comprises Pd, the solution (A) is made acid by sulfuric acid or phosphoric acid. Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) is however preferred.

10018868-030702

The solution (A) particularly preferred contains about 100 mg/l of NaBr, 10 mg/l of Br<sub>2</sub> and 10 g/l of orthophosphoric acid.

In general, the process is carried out with a small amount of supported catalyst of between 5 and 50 g per liter of solution (A). An amount of catalyst close to 10 g per liter of solution (A) is preferred.

The treatment temperature is in general between 10 and 80°C and preferably between 40 and 60°C.

The treatment time may vary between wide limits. This time may be between 1 and 12 hours and preferably between 4 and 8 hours.

After the treatment, the catalytic solid is separated from the aqueous solution (A) by any known means and then dried at a temperature of between 100 and 140°C and preferably close to 120°C. Usually, the drying is carried out at atmospheric pressure, for example by means of a fan oven.

Impregnation of the support may be carried out by any known means. Advantageously, the impregnation step consists in bringing the chosen support into contact with the most concentrated possible aqueous solution of the salt or salts of at least one metal from the group M so as to form a slurry. This contacting step may be carried out by adding the concentrated aqueous solution of metal salt(s), at room temperature, to a mixer containing the support. The mixing time depends in general on the amount of support employed, but for productivity reasons it is preferred,

after the metal solution has been added, to mix for about 0.5 to 3 hours.

After mixing and before the reduction step, the resulting slurry is preferably filtered, then drained and finally dried. To ensure maximum draining, it is recommended to carefully compress the filtered slurry. After draining, the impregnated support is dried preferably at a temperature of between 20 and 50°C. Advantageously, the drying is carried out under conditions conducive to slow crystallization and preferably in the absence of agitation. The drying time depends in general on the temperature and the pressure. It is usually between 1 and 7 days. As an indication in a vacuum oven heated to 40°C, 48 hours are enough to dry the impregnated and drained solid. The drying may also be carried out at room temperature for a week.

One particular method of preparing the supported catalyst based on at least one metal from the group M comprises, in succession, the following steps:

(a) bringing a support, selected from the group formed by silica, alumina, carbon and aluminosilicates, into contact with a concentrated aqueous solution of one or more salts of at least one metal from the group M so as to form a slurry;

(b) filtering, draining and then drying the slurry under conditions conducive to slow crystallization;

(c) reducing the solid dried in step (b);

---

(d) treating the solid reduced in step (c) with an aqueous acid solution (A) containing bromine and bromide ions; and

(e) filtering the solid treated in step (d) and drying it at a temperature of between 100 and 140°C.

The preferred operating conditions for each step of the preparation are the same as those described above. With regard to the reduction step, the experimental conditions already used in the prior art, for example US 5 128 114 and US 5 352 645, may be applied.

Any known means for helping the metal salts to dissolve, so as to obtain a concentrated aqueous solution for the impregnation step (a), may be used. The use of a few drops of acid, slight heating and ultrasonic stirring may especially be mentioned.

It is preferred to grind the dried solid from step (b) before subjecting it to the reduction step. In practice, the oven used for the reduction is firstly purged with nitrogen for a sufficient time, generally 15 and 60 minutes, then flushed with hydrogen before being heated to a temperature of between 250 and 350°C. The solid reduction time at the chosen temperature may be between 1 and 3 hours. After reduction, the oven is returned to room temperature and then purged with nitrogen.

A third subject of the invention is the process for direct manufacture of hydrogen peroxide from

10018868-030702



hydrogen and oxygen. This process is characterized in that the catalyst described and prepared above is used.

The catalyst may be used in a process for the direct manufacture of hydrogen peroxide both in a tube reactor and in a stirred reactor. It is most particularly suitable for the process in which hydrogen and oxygen are injected into the aqueous reaction mixture in the stirred reactor and oxygen is introduced into the continuous gas phase in the stirred reactor.

Advantageously, the catalyst may be used in a direct hydrogen peroxide manufacturing process in which the hydrogen and oxygen are injected into the lower part of the aqueous reaction mixture and oxygen is introduced into the continuous gas phase in the stirred reactor in an amount such that the composition of this continuous gas phase is outside the flammability range.

The catalyst has proved to be very beneficial when the stirred reactor is provided with several turbines arranged along a single vertical axis. When the hydrogen and oxygen are injected in the form of small bubbles into the lower part of the aqueous reaction mixture in proportions such that the ratio of the hydrogen molar flow rate to the oxygen molar flow rate is greater than 0.0416, a higher hydrogen peroxide productivity than that in the prior art is obtained.

The catalyst has proved to be particularly beneficial in a continuous direct hydrogen peroxide manufacturing process with recycling of the reactants, such as hydrogen.

10018868 "030702"

**EXPERIMENTAL PART**Preparation of the catalystsExample 1

The following were added at room temperature into 50 cm<sup>3</sup> of demineralized water:

- 0.33 g of PdCl<sub>2</sub> (Aldrich reference: 20,588-5);
- 0.021 g of H<sub>2</sub>PtCl<sub>6</sub> (Aldrich reference: 25,402-9);

and a few drops of 30% by weight of HCl in order to aid dissolution;

- 20 g of microporous silica Aldrich (reference 28,851-9) having the following characteristics:

mean particle size:	25 $\mu$ m
BET surface area:	500 m <sup>2</sup> /g
pore volume:	0.75 cm <sup>3</sup> /g
mean pore diameter:	60 Å

were placed in a glass beaker, stirred using a bar magnet. 50 cm<sup>3</sup> of the metal salt solution prepared above were then rapidly added.

After stirring for 1 hour 30 minutes at 25°C, a thick stock was obtained, which was filtered over a No. 3 glass frit and vacuum drained for 2 hours 30 minutes. The filter cake was placed in a crystallizer over a glass cloth and dried for 48 hours at 40°C in a vacuum oven. Next, the dried solid was reduced in a stream of 60 Nl/h of H<sub>2</sub> at 300°C for

1 hour 30 minutes and then cooled to room temperature over 6 hours.

The reduced solid was then treated at 40°C for 5 hours with 2000 cm<sup>3</sup> of a solution containing 100 mg/l of NaBr, 10 mg/l of Br<sub>2</sub> and 10 g/l of H<sub>3</sub>PO<sub>4</sub>.

Next, the resulting mixture was filtered and the catalyst dried for 24 hours in a fan oven at 120°C.

After analysis the catalyst contained 0.7% Pd and 0.03% platinum by weight.

#### Example 2

The procedure was as in Example 1, with the sole difference that the reduced solid was used directly as a catalyst without treatment with the aqueous brominated solution.

#### Example 3

After the silica was impregnated in Example 1, instead of filtering the stock and draining the filtered slurry, the stock was dried in a laboratory rotary evaporator (Heidolph with a 500 cm<sup>3</sup> fluted round-bottomed glass flask). The flask was rotated in an oil bath at 120°C in a vacuum of 40 mmHg. After evaporation, the solid was reduced and then treated as described in Example 1.

#### Example 4

The procedure was as described in Example 3 except that the solid after reduction was not treated with the aqueous brominated solution.

#### Example 5

The procedure was as described in Example 3 except that after impregnation the stock was left in the ambient air for 1 week instead of being dried in the rotary evaporator.

#### Example 6

The procedure was as described in Example 1 except that the Pd was replaced with Au.

#### Example 7

The procedure was as described in Example 1 except that the Pt was replaced with Ho.

#### Example 8

The procedure was as described in Example 1 except that the Pt was replaced with Au.

### Preparation of the hydrogen peroxide solution

#### General operating method

A chosen amount of aqueous reaction mixture and catalyst was introduced into a cylindrical reactor, having a total capacity of 1500 cm<sup>3</sup>, fitted with two or three flanged turbines 45 mm in diameter, with 4 vertical baffles and with a bundle of cooling tubes.

The aqueous reaction mixture was prepared by adding 12 g of  $\text{H}_3\text{PO}_4$ , 58 mg of NaBr and 5 mg of  $\text{Br}_2$  in 1000  $\text{cm}^3$  of demineralized water.

The reactor was pressurized by injecting oxygen into the continuous gas phase with a chosen flow rate. The pressure was kept constant by means of a pressure regulator. The liquid medium was raised to the chosen temperature by the circulation of thermostated water through the bundle of cooling tubes.

The stirring was set at 1900 rpm and oxygen and hydrogen were injected into the liquid phase at the center of the bottom turbine with chosen flow rates.

The flow rate and the hydrogen content of the gas mixture leaving the pressure regulator were measured. After the anticipated reaction time had elapsed, the feed of hydrogen and oxygen into the aqueous reaction mixture was cut and the injection of oxygen into the continuous gas phase was continued until the hydrogen in the latter disappeared. The oxygen feed was then cut and the reactor decompressed.

The aqueous hydrogen peroxide solution was weighed and separated from the catalyst by filtration over a Millipore® filter.

This solution was then assayed by iodometry in order to determine the  $\text{H}_2\text{O}_2$  concentration. The  $\text{H}_2\text{O}_2$  selectivity is defined as <sup>a percentage of</sup> the ratio of the number of moles of  $\text{H}_2\text{O}_2$  formed to the number of moles of  $\text{H}_2$  consumed.

10018868-030702

The degree of conversion is defined as being the <sup>percentage of</sup> ratio of the volume of  $H_2$  consumed to the volume of  $H_2$  injected.

The catalyst results for each trial are summarized in Table I.

10018858.030702

Table I

Trial No.	Catalyst example	REACTION MIXTURE		REACTION CONDITIONS							RESULTS		
		Catalyst Weight (g)	WORKING SOLUTION	P (bar)	Reaction Temp. (°C)	H <sub>2</sub> injected into the liquid phase (NL/h)	O <sub>2</sub> injected into the liquid phase (NL/h)	O <sub>2</sub> injected into the gas phase (NL/h)	Number of turbines	Time (h)	H <sub>2</sub> O <sub>2</sub> (%)	H <sub>2</sub> O <sub>2</sub> selectivity	H <sub>2</sub> Conversion (%)
			Weight (g)										
1	1	6	700	50	20	80	188	1760	2	3	17.5	97	42.0
2	1	6	700	50	20	80	188	1760	2	3	17.4	96	42.0
3	2	6	700	50	20	80	188	1760	2	3	16.2	85	45.0
4	3	6	700	50	20	80	160	1760	2	3	16.3	84	45.8
5	4	6	700	50	20	80	160	1760	2	3	15.4	82	44.0
6	1	6	700	50	41.2	120	240	2640	2	1	12.2	90	60.2
7	5	6	700	50	41.5	120	240	2640	3	1	12.4	86	64.3
8	1	8.5	1000	50	39.8	120	240	2640	3	1	10.6	90	72.5
9	6	8.5	1000	50	40.5	120	240	2640	3	1	6.4	54	71.6
10	7	8.5	1000	50	39.5	120	240	2640	3	1	7.8	76	61.6
11	8	8.5	1000	50	40	120	240	2640	3	1	7.9	73	65.6

## CLAIMS

1. A process for preparing a supported catalyst based on at least one metal from the group M formed by palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold, comprising, in succession, a step of impregnating a solution based on one or more salt(s) of at least one metal from the group M on a support, and a reduction step, characterized in that, after the reduction step, the catalyst is subjected to a treatment with an aqueous acid solution (A) containing bromine and bromide ions.

2. The process as claimed in claim 1, characterized in that the concentration of bromide ions in the aqueous solution (A) is between 20 and 200 mg/l and preferably between 20 and 100 mg/l.

3. The process as claimed in either of claims 1 and 2, characterized in that the bromine concentration is between 2 and 20 mg/l and preferably between 2 and 10 mg/l.

4. The process as claimed in any one of claims 1 to 3, characterized in that the pH of the aqueous solution (A) is between 1 and 3.

5. The process as claimed in any one of claims 1 to 4, characterized in that the treatment temperature is between 10 and 80°C and preferably between 40 and 60°C.

6. The process as claimed in any one of claims 1 to 5, characterized in that after the

10018868 030702



treatment the catalytic solid is separated from the solution A and then dried at a temperature of between 100 and 140°C.

7. The process as claimed in any one of claims 1 to 6, characterized in that, after impregnation and before the reduction step, the resulting slurry is filtered, then drained and finally dried.

8. The process as claimed in claim 7, characterized in that the drying is carried out under conditions conducive to slow crystallization.

9. A supported catalyst based on at least one metal selected from the group M formed by palladium, platinum, ruthenium, rhodium, iridium, osmium, holmium and gold, the content of a selected metal being between 0.1 and 10% by weight of the catalyst, characterized by clusters of crystallized metal or metals having a size of between 0.1 and 20  $\mu\text{m}$  and preferably between 0.1 and 10  $\mu\text{m}$ .

10. The process or catalyst as claimed in one of claims 1 to 9, characterized in that palladium and gold are advantageously selected.

11. The process or catalyst as claimed in one of claims 1 to 9, characterized in that the catalyst is a supported bimetallic catalyst in which the minority metal represents between 0.001 to 0.1% by weight of the catalyst.

10018868 030702

12. The process or catalyst as claimed in claim 11, characterized in that the minority metal is platinum.

13. The process or catalyst as claimed in one of claims 1 to 12, characterized in that the support is a silica having a BET specific surface area of preferably greater than 200 m<sup>2</sup>/g.

14. A process for the direct manufacture of hydrogen peroxide from hydrogen and oxygen, characterized in that a catalyst as claimed in one of claims 1 to 13 is used.

10018868 1030702

DECLARATION FOR NON-PROVISIONAL PATENT APPLICATION\*

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below at 201 et seq. beneath my name.

I believe I am the original, first and sole inventor if only one name is listed at 201 below, or an original, first and joint inventor if plural names are listed at 201 et seq. below, of the subject matter which is claimed and for which a patent is sought on the invention entitled

SUPPORTED METAL CATALYST, PREPARATION AND APPLICATIONS FOR DIRECTLY MAKING HYDROGEN PEROXIDE

and for which a patent application:

☐ is attached hereto and includes amendment(s) filed on (if applicable)

☒ was filed in the United States on December 19, 2001 as Application No. 10/018,868 with amendment(s) filed on December 19, 2001

☒ was filed as PCT international Application No. PCT/FR00/01552 on June 7, 2000 and was amended under PCT Article 19 on (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

EARLIEST FOREIGN APPLICATION(S), IF ANY, FILED PRIOR TO THE FILING DATE OF THE APPLICATION			
APPLICATION NUMBER	COUNTRY	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
99/09260	France	July 16, 1999	YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>
99/10310	France	August 9, 1999	YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information known to me which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

NON-PROVISIONAL APPLICATION SERIAL NO.	FILING DATE	STATUS		
		PATENTED	PENDING	ABANDONED

\* for use only when the application is assigned to a company, partnership or other organization.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

201	FULL NAME OF INVENTOR	LAST NAME Devic	FIRST NAME Michel	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY Saint Foy les Lyon	STATE OR FOREIGN COUNTRY France	COUNTRY OF CITIZENSHIP France	
	POST OFFICE ADDRESS	STREET 22, rue Georges Clémenceau	CITY Saint Foy les Lyon	STATE OR COUNTRY France	ZIP CODE F-69110
	SIGNATURE OF INVENTOR 201 <i>Michel Devic</i>			DATE 21 February 2002	
202	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 202			DATE	
203	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 203			DATE	
204	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 204			DATE	
205	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	STREET	CITY	STATE OR COUNTRY	ZIP CODE
	SIGNATURE OF INVENTOR 205			DATE	